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Chemical Effects Associated with β -Decay Process. III.
The Chemical Behavior of ^{144}Pr Decayed from
 $^{144}\text{Ce(III)-EDTA}$ Complexes in the Solid Phase

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The chemical behavior of ^{144}Pr formed by the β -decay of ^{144}Ce in crystals of $^{144}\text{Ce(III)-EDTA}$ complexes has been investigated by means of ion-exchange techniques. The initial yield of $^{144}\text{Pr}^{3+}$ ion, which reflects the distribution of the ^{144}Pr atoms in the crystal, is independent of the dissolving condition, but is affected by the amount of hydration in the crystal. Abnormal behavior of ^{144}Pr atom has not been found in the ammonium salt. These results suggest that in the solid phase $^{144}\text{Pr}^{3+}$ or its precursor may be produced as a result of multiple charging of the daughter following electron shake-off and internal conversion of γ -rays.

A number of studies have been carried out on the chemical consequences of molecules resulting

from the β -decay of a constituent atom. The chemical behavior of the radioactive daughter atom depends on its recoil energy, charge and electronic excitation resulting from the change in nuclear charge. Therefore, a change in oxidation

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state of the radioactive daughter atom has become of interest. Cerium-praseodymium-144 possesses several advantages in its nuclear and chemical properties for a study of the chemical behavior of the radioactive daughter atoms formed by β -decay. Several authors¹⁻⁴⁾ reported the chemical behavior of ^{144}Pr in this system previously.

In an earlier paper,²⁾ the present authors investigated the chemical behavior of ^{144}Pr formed by β -decay of the ^{144}Ce labeled cerium(III)-ethylenediaminetetraacetate ($^{144}\text{Ce(III)-EDTA}$) complex in the liquid phase. The results suggested that an increase in the nuclear charge of ^{144}Pr plays the most important role in the process of β -decay of $^{144}\text{Ce(III)-EDTA}$ complex, and leads to the disruption of the complex molecule *via* intramolecular electron-transfer. The kinetic study³⁾ indicated the existence of an intermediate, produced as a result of β -decay.

The present investigation was undertaken in the solid phase to obtain further information on the chemical behavior of ^{144}Pr formed by β -decay of $^{144}\text{Ce(III)-EDTA}$ complex.

Experimental

Chemicals. Reagents used are as reported previously.²⁾

The sodium salt of $^{144}\text{Ce(III)-EDTA}$ complex ($\text{Na-}^{144}\text{CeY} \cdot m\text{H}_2\text{O}$) was synthesized by the reaction of cerium(III) nitrate and the disodium salt of EDTA ($\text{Na}_2\text{H}_2\text{Y}$) in aqueous solution at pH 6.5. The solution was concentrated by evaporation and placed in an ice bath. The resulting crystalline product was recrystallized from a 90 per cent ethanol solution. In the process of recrystallization, the carrier-free ^{144}Ce was added. The ammonium salt of $^{144}\text{Ce(III)-EDTA}$ complex ($\text{NH}_4\text{-}^{144}\text{CeY} \cdot 5\text{H}_2\text{O}$) was prepared in a similar way, except that the ammonium salt of EDTA was used instead of the sodium salt.

The solid chelates were analyzed for Ce^{3+} and Y^{4-} , and then the hydration number of the crystal calculated by difference.⁵⁾

Apparatus and Procedures. The solid complex, allowed to stand for more than three hours at 0°C , was dissolved in a 0.4 M sodium acetate buffer solution. The ionic strength was adjusted to 0.5 with sodium chloride. The final concentration of the complex ion was 1×10^{-3} M. The solution was placed in a bath at the desired temperature. To separate the free-ion, an aliquot of the solution was withdrawn through a Dowex 50W-X8 column (8 mm ϕ \times 10 mm, 50—100

mesh). The resin used had been treated with a proper buffer solution before use. All procedures were performed at $0 \pm 0.5^\circ\text{C}$.

The yield of the free-ion fraction was obtained by counting the γ -activities of both the resin phase and the combined effluents, as described previously.²⁾ The pH of the solution was measured with a glass-electrode pH meter to an accuracy of ± 0.01 .

Results

It was found that the yields of $^{144}\text{Pr}^{3+}$ ion, which represent the extent of molecular disruption due to β -decay of $^{144}\text{Ce(III)-EDTA}$ complex increase or decrease with time after dissolution. As an example, Fig. 1 shows an increase in the apparent

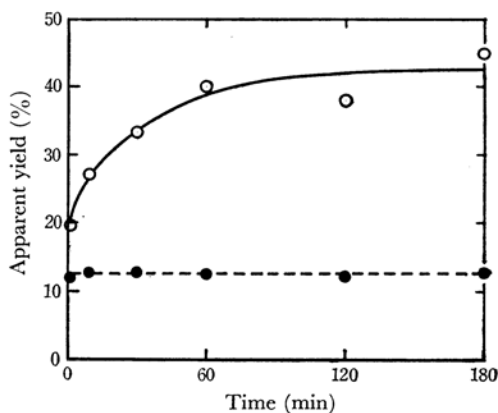


Fig. 1. Apparent yield of $^{144}\text{Pr}^{3+}$ and $^{144}\text{Ce}^{3+}$ in $\text{Na-}^{144}\text{CeY} \cdot 7\text{H}_2\text{O}$ dissolving at pH 7.08.

○: $^{144}\text{Pr}^{3+}$; ●: $^{144}\text{Ce}^{3+}$

yield of $^{144}\text{Pr}^{3+}$ ion up to the plateau value in a neutral solution. It should be noticed that the cerium is also adsorbed to some extent on the resin under this condition. Since the adsorbability of the cerium(III) ion is independent of the lapse of time after dissolution, it is ascribed to the transfer of the EDTA complex to the cationic fraction on separation. Thus, the net yield of $^{144}\text{Pr}^{3+}$ ion formed by β -decay of $^{144}\text{Ce(III)-EDTA}$ complex could be obtained by subtraction of the normal distribution from the apparent yield. Figure 2 shows the net yield curves for $^{144}\text{Pr}^{3+}$ ion at various pH values.

The plateau yield of $^{144}\text{Pr}^{3+}$ ion increases in the neutral regions, pH 6.5, whereas it decreases in low pH regions. The distribution of the plateau yields of $^{144}\text{Pr}^{3+}$ ion as a function of pH is shown in Fig. 3.

The initial yield of $^{144}\text{Pr}^{3+}$ ion, which is defined as the yield just after dissolution of the crystal, could be obtained by extrapolation of the yield of $^{144}\text{Pr}^{3+}$ ion to zero time. The initial yield of $^{144}\text{Pr}^{3+}$ ion for a given crystal is quite independent

1) R. R. Edwards and C. D. Coryell, TID-13363 (1961).

2) T. Shiokawa, H. Kudo and T. Omori, This Bulletin, **38**, 1340 (1965).

3) T. Shiokawa and T. Omori, *ibid.*, **38**, 1892 (1965).

4) P. Glentworth and B. Wisell, "Chemical Effects of Nuclear Transformations (Proc. Symp. Vienna)," Vol. II. IAEA, Vienna (1965), p. 483.

5) N. P. Kusakina and E. M. Yakinets, *Russ. J. Inorg. Chem.*, **10**, 457, 459 (1965).

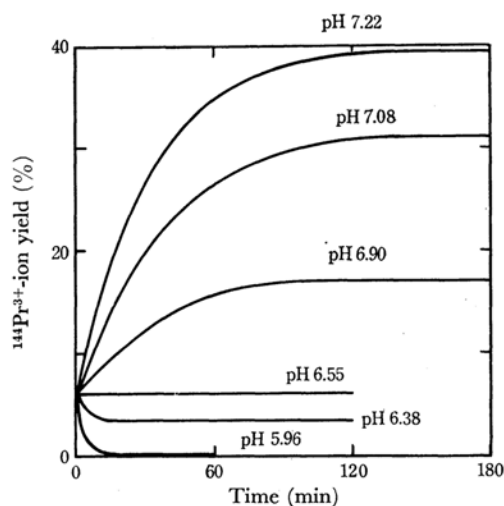


Fig. 2. Yield of $^{144}\text{Pr}^{3+}$ ion in $\text{Na}^{144}\text{CeY} \cdot 7\text{H}_2\text{O}$ dissolving at various pH.

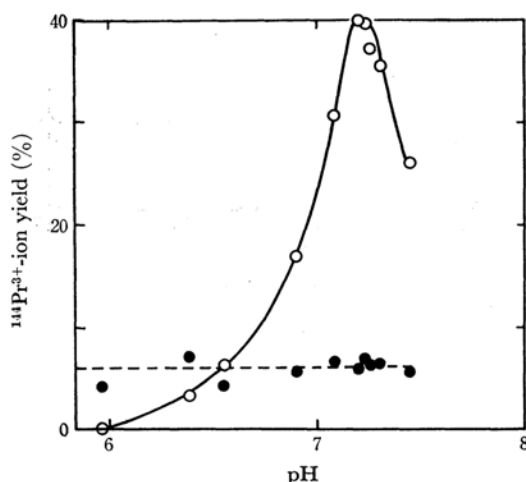


Fig. 3. Yield of $^{144}\text{Pr}^{3+}$ ion in $\text{Na}^{144}\text{CeY} \cdot 7\text{H}_2\text{O}$ as a function of pH of the aqueous solution.

○: plateau yield; ●: initial yield

of the dissolving condition of the aqueous solution, while it is significantly affected by the hydration number of the crystal. The results are summarized in Table 1.

TABLE I. INITIAL YIELD OF $^{144}\text{Pr}^{3+}$ ION RESULTING FROM β^- -DECAY OF ^{144}Ce IN THE CRYSTAL OF EDTA COMPLEXES

Crystal	Initial yield (%)
$\text{Na}^{144}\text{CeY} \cdot 4\text{H}_2\text{O}$	3.9 ± 0.4
$\text{NH}_4^{144}\text{CeY} \cdot 5\text{H}_2\text{O}$	4.7 ± 0.4
$\text{Na}^{144}\text{CeY} \cdot 6\text{H}_2\text{O}$	5.4 ± 0.4
$\text{Na}^{144}\text{CeY} \cdot 7\text{H}_2\text{O}$	6.0 ± 0.4
$\text{Na}^{144}\text{CeY} \cdot 12\text{H}_2\text{O}$	9.1 ± 0.3

Discussion

The general aspect of the distribution curve of the plateau yields of $^{144}\text{Pr}^{3+}$ ion as seen in Fig. 3 is similar to that observed in the liquid system.³⁾ Thus, the plateau yield of $^{144}\text{Pr}^{3+}$ ion could be explained by application of the mechanism proposed previously^{2,3)}; that is, tetrapositive ^{144}Pr produced as a result of simple β^- -decay of $^{144}\text{Ce}(\text{III})$ -EDTA complex would be reduced to a tripositive state by intramolecular electron-transfer. The tripositive praseodymium still forms an intermediate complex with an oxidation product of EDTA, but is liberated by proton attack as the free-ion form.

In a given crystal, however, the initial yields obtained under different dissolving conditions are essentially constant, as shown in Fig. 2. From Table I, one can also see that the initial yield of $^{144}\text{Pr}^{3+}$ ion increases with hydration number of the crystal. These results strongly suggest the existence of a chemical species other than the intermediate in the solid state; viz., $^{144}\text{Pr}^{3+}$ ion or a precursor, which transforms to $^{144}\text{Pr}^{3+}$ ion just after dissolution. In the solid phase, the intermediate is thought to be rather stable, and its contribution to the initial yield of $^{144}\text{Pr}^{3+}$ ion would be of minor importance. A possible alternative explanation could be that the initial molecular ion, $^{144}\text{Pr}(\text{IV})$ -EDTA, can exist in the crystal, or that it can be stabilized to $^{144}\text{Pr}(\text{III})$ -EDTA complex by intermolecular electron-transfer.

As pointed out above, the daughter atom formed by β^- -decay will have a positive charge of one unit higher than the parent atom, and tetravalent ^{144}Pr may cause the disruption of EDTA complex via an intermediate. On the other hand, further ionization resulting from electron shake-off will take place, so that the daughter atom will have a positive charge greater than +5. In addition, multiple charging of ^{144}Pr will take place in consequence of the internal conversion of γ -rays. The yield is estimated to be 13% from the internal conversion coefficient.⁶⁾

In comparison with theoretical estimates, relatively small values for the initial yields predict that all multiply charged species do not transform to the free praseodymium ion or its precursor. However, it should be noticed that in the solid phase the chemical effect associated with the β^- -decay of ^{144}Ce is mainly attributed to the multiple

6) I. Pullman and P. Axel, *Phys. Rev.*, **102**, 1366 (1956).

7) J. L. Hoard, E. Willstandter and J. V. Silverton, *J. Am. Chem. Soc.*, **87**, 1611 (1965).

8) For example, R. E. Cleary, W. H. Hamill and R. R. Williams, *J. Am. Chem. Soc.*, **74**, 4675 (1952); K. J. McCallum and A. G. Maddock, *Trans. Faraday Soc.*, **49**, 1150 (1953); G. Harbottle, *J. Chem. Phys.*, **22**, 1083 (1954).

charging of the daughter atoms following electron shake-off and Auger processes, so long as it is discussed in terms of the initial yield of $^{144}\text{Pr}^{3+}$ ion.

In order to understand the fate of the ^{144}Pr atom in the solid phase, it is very important to investigate the effect of the hydration number of the solid complex on initial yield. On the basis of a structural investigation of rare earth-EDTA complexes,⁷⁾ it seems reasonable to estimate that the structural formula of the sodium salt of $^{144}\text{Ce}(\text{III})$ -EDTA complex is $\text{NaCeY}(\text{O}_2\text{H})_4 \cdot m\text{H}_2\text{O}$. Since the hydration numbers of the solid complexes used in this experiment varied from four to twelve, the complexes have fundamentally identical structures, being different in outer-sphere hydration. Accordingly, a linear increase in initial yields with hydration numbers of the EDTA complexes would suggest that water molecules in the outer-sphere affect either the decomposition of the EDTA complex resulting from the highly charged ^{144}Pr

ion or the stabilization reaction of liberated ^{144}Pr ion in the solid phase.

It appeared of interest to study the initial yield of $^{144}\text{Pr}^{3+}$ ion in the ammonium salt of $^{144}\text{Ce}(\text{III})$ -EDTA complex. In the (n,γ) reaction, retentions of the ammonium salts are always abnormally low.⁸⁾ No discrepancy, however, has been found in this system, as seen in Table 1. This fact suggests that because of the low recoil energy of the β^- -decay of ^{144}Ce , ^{144}Pr could not interact with ammonium ion.

The chemical consequences of the β^- -decay of the $^{144}\text{Ce}(\text{III})$ -EDTA complex has been discussed hitherto mainly from the point of view of thermodynamical instability of the daughter molecular ion.^{2,3)} However, the present investigation in the solid phase reveals that the multiple charge of the daughter plays an important role in determining the chemical behavior of the ^{144}Pr atom.